



# Electrochemical CH<sub>4</sub> oxidation into acids and ketones on ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> quasi-solid solution nanowire catalyst

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## ABSTRACT

Efficient utilization of abundant methane (CH<sub>4</sub>) from natural gas remains a major catalysis challenge. One recommended strategy is to convert methane into liquid fuels, such as alcohols, ketones and acids, but most processes usually proceed through high-temperature routes. Here, we employ a ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> quasi-solid solution catalyst as the electrochemical anode for partial methane oxidation. Without high temperature, noble metal catalysts and expensive oxidants, this quasi-solid solution anode produces propionic acid, acetic acid and acetone. After the analysis of the products, we demonstrate that the intermediate products from partial methane oxidation, 1-propanol, acetaldehyde and 2-propanol, are further oxidized into propionic acid, acetic acid and acetone, respectively. Long-term stable production via methane oxidation is a new strategy for the electrochemical conversion of organic chemicals.

## 1. Introduction

Methane (CH<sub>4</sub>) is a major component of natural gas with lower carbon dioxide emissions when it is combusted. However, the emission of CH<sub>4</sub> cause the greenhouse effect with 30 times of CO<sub>2</sub> [1]. During the exploitation process of CH<sub>4</sub> from shale gas and marsh gas, the CH<sub>4</sub> emission would cause more serious environmental pollution and climate change. Thus, a suitable method to convert CH<sub>4</sub> to liquid fuels could solve aforementioned problems and, more importantly which will provide more value-added materials from CH<sub>4</sub>. Numerous efforts have been made to directly convert CH<sub>4</sub> into liquid fuels, such as alcohols and ketones, as value-added materials [2–5]. Unfortunately, the proposed cyclic gas-phase conversion systems need high temperatures (> 200°) to activate CH<sub>4</sub> to produce CH<sub>3</sub>OH due to the strength of the CH<sub>3</sub>-H bond (435 kJ mol<sup>-1</sup>) [6,7]. An alternative method, the liquid-phase conversion strategy, employs milder reaction conditions; however, high temperatures (180 °C) with strongly acidic media or highly oxidative and expensive hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) should be employed [8–11].

Electrochemical redox reactions have been employed to breakdown various stable chemicals, such as water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>). [12–14] In particular, in the electrochemical reduction reaction of CO<sub>2</sub>, various kinds of higher alcohol products can be obtained

depending on the catalyst used [15,16]. We have previously reported that electrochemical oxidation of CH<sub>4</sub> using a Co<sub>3</sub>O<sub>4</sub>/ZrO<sub>2</sub> mixture in an aqueous electrolyte at room temperature has been proven as an appropriate method with simple instruments to generate C1 to C3 liquid fuels [17]. However, the nonselective production of 1-propanol and 2-propanol makes it difficult to envisage a commercial-level process based on this method [17].

Applied with a relatively small bias, highly efficient and selective incorporation of CH<sub>4</sub> into higher alcohol products would represent substantial progress for more reliable and economically viable processes for a CH<sub>4</sub> conversion into value-added products. Thus, we designed a ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> quasi-solid solution nanowire catalyst with porous structure through a simple hydrothermal method to realize sufficient supplementation of the oxidizing agent source during the oxidation process. The fabrication process of the ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> quasi-solid solution nanowire catalyst and its function for CH<sub>4</sub> electrochemical oxidation are shown in Fig. 1. According to our experimental results, stable oxygenates, such as propionic acid, acetic acid and acetone, were produced, and the methane oxidation conversion efficiency achieved after 20 h was 47.5%.

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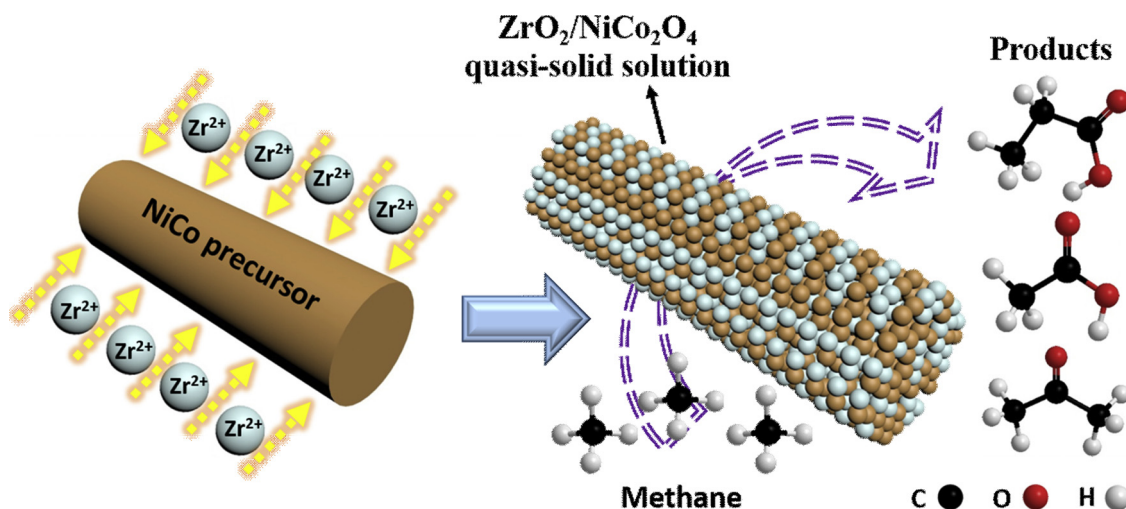


Fig. 1. The fabrication process of the  $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  quasi-solid solution catalyst and its function for  $\text{CH}_4$  electrochemical oxidation.

## 2. Experimental section

### 2.1. Electrocatalyst synthesis

All chemicals were used as received without further treatment. The  $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  quasi-solid solution catalysts were synthesized using a hydrothermal method. For the 0.5- $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  sample, 0.322 g  $\text{NiCl}_2$  (98%, Sigma Aldrich), 1.19 g  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$  ( $\geq 98\%$ , Sigma Aldrich), 0.117 g  $\text{ZrCl}_4$  ( $\geq 99.5$ , Sigma Aldrich), 0.54 g urea (99.0–100.5%, Alfa Aesar), and 0.728 g hexadecyl trimethyl ammonium bromide ( $\geq 99\%$ , Acros Organics) were dissolved in 40 ml deionized (DI) water with vigorous stirring for 30 min, followed by sonication for 1 h to ensure homogeneous mixing. Then, the solution was transferred to a 60 ml autoclave container and heated at 120 °C for 48 h. After that, the powder was collected by centrifugation and washed with DI water 6 times to eliminate all residuals. Then, the precursor 0.5- $\text{Zr}:\text{NiCo}$  was obtained. The 0.5- $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  sample was obtained after thermal annealing of the precursor at 500 °C for 3 h. To obtain the different ratios of the  $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  samples, the amount of  $\text{ZrCl}_4$  was changed to 0.047 g for 0.2- $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$ , 0.234 g for 1.0- $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$ , and 0.468 g for 2.0- $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  without changing the other conditions. For comparison, pure  $\text{NiCo}_2\text{O}_4$  was prepared. Pure  $\text{NiCo}_2\text{O}_4$  was synthesized by the same method used for the  $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  synthesis without the addition of  $\text{ZrCl}_4$ .

### 2.2. Electrocatalytic performance measurements

LSV measurements were conducted to compare the electrocatalytic performances of  $\text{ZrO}_2/\text{NiCo}_2\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  in a two-electrode system using a potentiostat (CH Instrument, CHI 660) with a glassy carbon electrode as the working electrode, Pt foil as the counter electrode and a 0.5 M  $\text{Na}_2\text{CO}_3$  solution as the electrolyte. All working electrodes were prepared by dispersing powder samples in DI water at a concentration of 3 mg  $\text{ml}^{-1}$  and then dropping 20  $\mu\text{l}$  of the dispersed solution on the surface of the glassy carbon electrode (area = 0.07  $\text{cm}^2$ ). After drying, a 5% Nafion 117 solution (Sigma Aldrich) was dropped on the surface of the electrode to cover the powder sample and form a surface film. Before each LSV measurement, the electrolyte was bubbled with Ar (99.9999%) or  $\text{CH}_4$  (99.9999%) for 1 h to prepare the Ar- or  $\text{CH}_4$ -saturated electrolyte.

### 2.3. Electrochemical $\text{CH}_4$ oxidation reaction

The electrochemical oxidation of  $\text{CH}_4$  was conducted in a two-electrode system, employing graphite foil (Alfa) as the working

electrode, Pt foil as the counter electrode and 30 ml of a 0.5 M  $\text{Na}_2\text{CO}_3$  solution as the electrolyte. The reactor was a closed cell with an approximately 395 ml gas-phase volume. The working electrode was prepared by dispersing the powder samples in DI water with a concentration of 3 mg  $\text{ml}^{-1}$  and then dropping 5.7 ml of the dispersed solution on the surface of the graphite foil (area = 20  $\text{cm}^2$ ). After drying, 1.5 ml of a 5% Nafion 117 solution was dropped to cover the sample on the graphite foil, followed by drying the sample at room temperature. Before the electrochemical reaction, the electrolyte was bubbled with  $\text{CH}_4$  for 1 h to remove the oxygen and fill the space in the reaction instrument. After that, the instrument was quickly closed to prevent gas emission. Then, the electrochemical oxidation of  $\text{CH}_4$  was conducted at 2.0 V vs. Pt for 5 h, 12 h and 20 h. The reaction temperature was controlled by water bath with room temperature, which was maintained at 25 °C.

### 2.4. Characterizations

The morphology analysis was carried out using field-emission scanning electron microscopy (FESEM, JEOL-7800 F) and transmission electron microscopy (TEM, JEM-F200). XRD patterns were measured using SmartLab in a Bragg-Brentano geometry. XPS data were obtained from a K-alpha instrument (Thermo Scientific Inc., UK).  $^1\text{H}$ -NMR was conducted using an Advance III HD 400 400 400 MHz FT-NMR instrument (Bruker Biospin), and the samples were prepared by mixing 0.4 ml of the product solution with 0.2 ml  $\text{D}_2\text{O}$ . The amount of methane was determined using a 7890B GC instrument (Agilent Technologies).

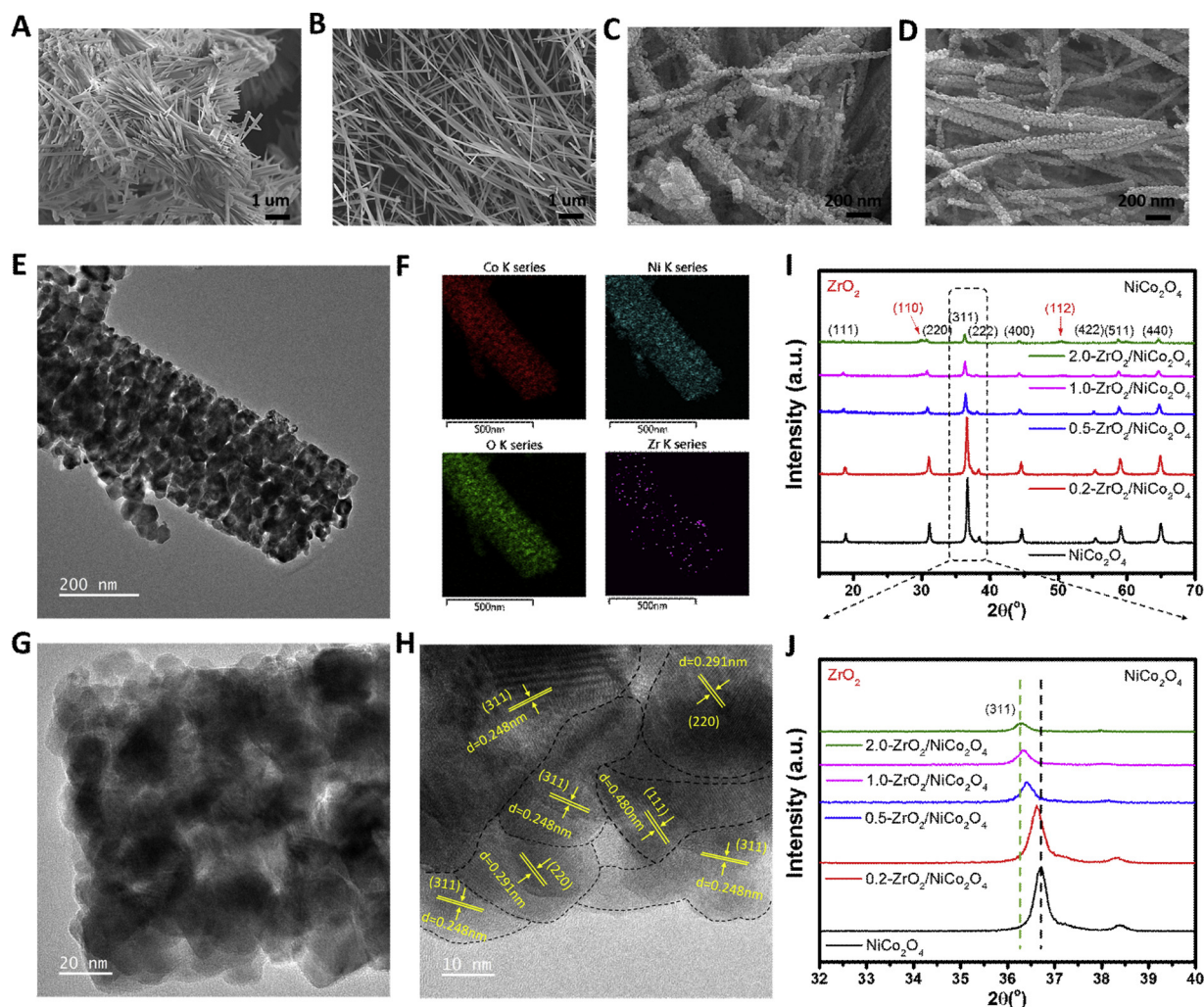
## 3. Results and discussion

Noble metals have been extensively explored for methane conversion [18–20]. However, their high cost and scarcity restrict their applications in industrial manufacturing. Instead, transition metal oxides have received more attention due to their abundance and relatively high catalytic activity [21], which depends on their reducible properties. Reducible oxides are characterized by their oxygen exchange capability via a relatively easy route. The absence of oxygen, generally as an oxygen vacancy, results in excess electrons that are redistributed on empty cation levels, which give rise to high lattice oxygen mobility, resulting in catalytic oxidation activity [22,23]. Among these reducible oxides, cobalt oxide ( $\text{Co}_3\text{O}_4$ ), a spinel oxide that consists of  $\text{Co}^{2+}$  at tetrahedral sites and  $\text{Co}^{3+}$  at octahedral sites in its lattice, has attracted much attention for methane oxidation applications. The relatively weak Co-O bonds allow easy production of oxygen vacancies under mild conditions, and the oxide is resistant to corrosion in alkaline media

[22–27]. Application of only 0.23 eV on the surface of  $\text{Co}_3\text{O}_4$  can realize oxygen vacancy migration [28]. Comparing to  $\text{Co}_3\text{O}_4$ , nickel cobalt oxide ( $\text{NiCo}_2\text{O}_4$ ) has been demonstrated to perform higher catalytic activity for chemical redox reactions [29–31]. During the formation of  $\text{NiCo}_2\text{O}_4$ , Ni cations are well integrated into the  $\text{Co}_3\text{O}_4$  crystal lattice due to the high oxygen vacancy density on  $\text{Co}_3\text{O}_4$  surface, and the atomic scale mixture with Ni cations [24,32] causes  $\text{NiCo}_2\text{O}_4$  to have the same spinel structure as  $\text{Co}_3\text{O}_4$ . DFT (density functional theory) calculations have been conducted to investigate the active sites of  $\text{NiCo}_2\text{O}_4$  for the dissociation of the first C–H bond in the primary  $\text{CH}_4$  oxidation process [27]. The calculation results suggest that Ni atoms on the surface of  $\text{NiCo}_2\text{O}_4$  have a much lower activation barrier for dissociating  $\text{CH}_4$  to  $\text{CH}_3$  than the Co atoms, illustrating the Ni cations as active sites in  $\text{NiCo}_2\text{O}_4$  for  $\text{CH}_4$  electrochemical oxidation. After the first activation of  $\text{CH}_4$ , the  $\text{CH}_3$  species will couple with lattice oxygen atoms to form  $\text{CH}_3\text{O}$  species, which are important intermediates to produce liquid fuels. Moreover, the binding energy of  $\text{CH}_2$  species on Ni cations is too low to realize further dehydrogenation of  $\text{CH}_3$ , resulting in the formation of stable  $\text{CH}_3\text{O}$  species [27]. Because of the high activity and low cost of  $\text{NiCo}_2\text{O}_4$ ,  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  could be a very promising catalyst for electrochemical catalytic  $\text{CH}_4$  oxidation due to the high catalytic activity from  $\text{NiCo}_2\text{O}_4$  and good oxygen source delivery from  $\text{ZrO}_2$ .

The  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  quasi-solid solution catalyst was synthesized by a hydrothermal method (details in the experimental section). The morphologies of the NiCo and Zr:NiCo precursors with different Zr

ratios can be observed from the SEM (scanning electron microscopy) images (Fig. 2 and S1). The precursors with different ratios are denoted as NiCo, 0.2-Zr:NiCo, 0.5-Zr:NiCo, 1.0-Zr:NiCo and 2.0-Zr:NiCo. The NiCo precursor (Fig. 2a) showed aggregated nanostructures consisting of short nanowires. Fig. S1 shows the structural variation that occurred with the addition of Zr atoms in the precursors, but the nanowire morphology remained. The length of the nanowires increased with the addition of Zr atoms. The 0.5-Zr:NiCo precursor (Fig. 2b) showed the most uniform morphology of the samples and a more elongated 1D morphology than the pure NiCo precursor; this sample also showed the best performance for  $\text{CH}_4$  oxidation. However, with the increased Zr content in 1.0-Zr:NiCo and 2.0-Zr:NiCo, the nanowire diameters increased and additional small particles were present on the surface due to  $\text{ZrO}_2$  crystals precipitating from the quasi-solid solution. After high-temperature annealing of the precursors, the final samples were obtained as  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  with different Zr ratios, which were denoted as 0.2- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ , 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ , 1.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  and 2.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ . Their morphologies were observed in SEM images, as shown in Figs. 2 and S2. During high-temperature annealing, the precursors changed to porous nanowires consisting of small nanoparticles. Pure  $\text{NiCo}_2\text{O}_4$  (Fig. 2c) consisted of porous nanowires that were partially broken due to the aggregated state of the NiCo precursor. However, porous 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  well maintained the nanowire structure and had a highly disperse nature, which contributed to its good catalytic ability. For the 1.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  and

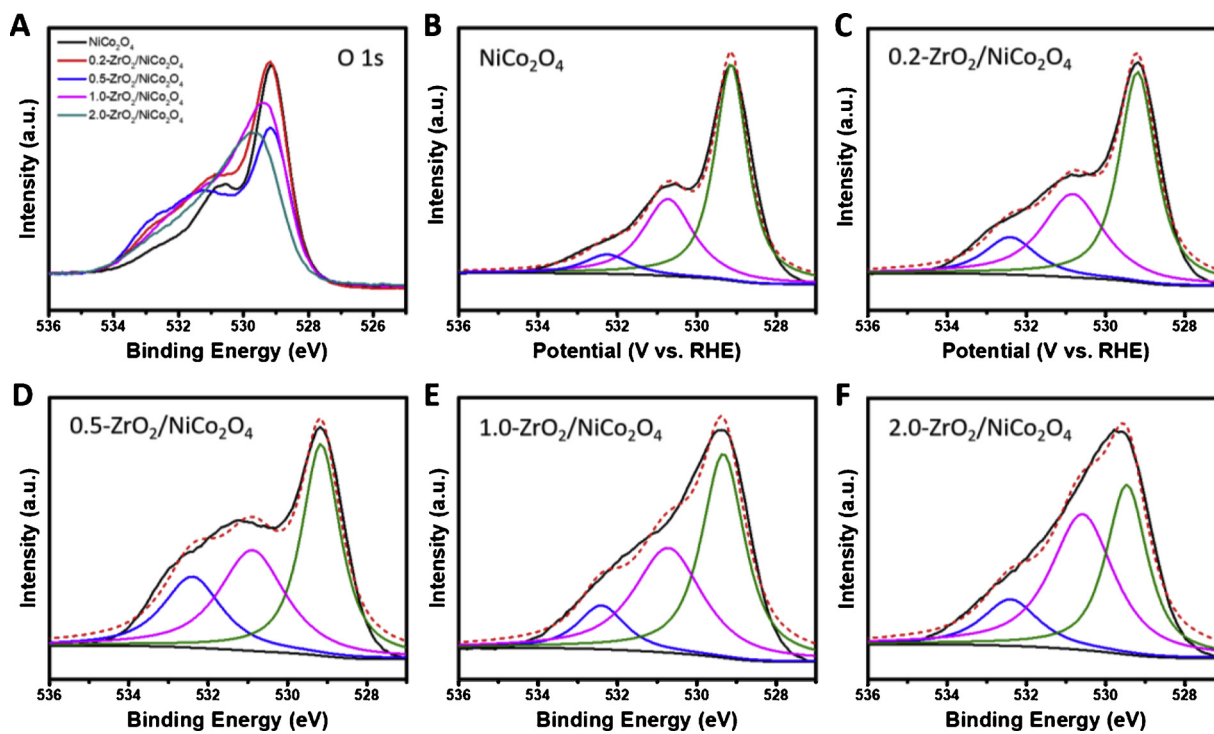


**Fig. 2.** SEM images of the (a) NiCo precursor, (b) 0.5-Zr:NiCo precursor, (c)  $\text{NiCo}_2\text{O}_4$  and (d) 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ . (e) TEM image and (f) element mapping of 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ . (g, h) High-resolution TEM images of 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ . (i, j) XRD patterns of  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  quasi-solid solution samples.



**Table 1**BET analysis of synthesized of  $\text{NiCo}_2\text{O}_4$ ,  $0.2\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$ ,  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$ ,  $1.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  and  $2.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$ .

Sample	$\text{NiCo}_2\text{O}_4$	$0.2\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$	$0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$	$1.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$	$2.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$
Specific surface area ( $\text{m}^2/\text{g}$ )	11.065	14.939	13.574	18.375	28.319

**Fig. 3.** (a) Overlapped and (b–f) deconvoluted O 1s XPS signals of  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  quasi-solid solution samples.

$2.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  samples (Fig. S2), the nanoparticle size increased with large isolated particles, which were exsolute  $\text{ZrO}_2$  particles. The destruction of the structure integrality by exsolute  $\text{ZrO}_2$  may destroy the quasi-solid solution balance and thereby reduce the catalytic performance of  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples for  $\text{CH}_4$  oxidation.

The nitrogen physisorption measurements (BET) have been conducted and shown in Table 1. From the BET analysis,  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples showed enlarged specific surface area when compared to the  $\text{NiCo}_2\text{O}_4$  sample due to the addition of  $\text{ZrO}_2$  component and the aggregative state of  $\text{NiCo}_2\text{O}_4$  itself, which can be confirmed from Figs. S1 and S2. For the  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples,  $1.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  and  $2.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  show increased specific surface area according to the increase of  $\text{ZrO}_2$  component amount. These two samples have relatively short nanorods structure and large diameter with additional  $\text{ZrO}_2$  crystals precipitating from the quasi-solid solution, which should be responsible for the increased specific surface area. In addition, the  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  sample shows relatively smallest specific surface area among the  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples, which should be ascribed to the well integration of  $\text{ZrO}_2$  into  $\text{NiCo}_2\text{O}_4$  to form the optimized quasi-solid solution.  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  presents superior uniformity with long nanorods structure as shown in Figs. S1 and S2.

TEM (transmission electron microscopy) measurements were used to investigate the crystal structures of  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$ , as shown in Fig. 2e. The  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  nanowires has cross-connected uniform particles with a 20–50 nm size. The dissolution of  $\text{ZrO}_2$  into the  $\text{NiCo}_2\text{O}_4$  crystalline structure created homogeneous small particles, as shown in the TEM image, and this result is consistent with the element mapping results shown in Fig. 2f, demonstrating the quasi-solid solution state of  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$ . From the high-resolution TEM (HR-TEM) images (Fig. 2g and h), the cross-connected structure of each

small particle can be clearly observed. The lattice constants of  $\text{NiCo}_2\text{O}_4$  are 0.248 nm, 0.291 nm and 0.480 nm, corresponding to the (311), (220) and (111) facets, respectively. The particles with different facets are separated by dashed lines in the HR-TEM image. Meanwhile, the  $\text{ZrO}_2$  crystal could not be found based on its lattice constant, indicating a solid solution of  $\text{ZrO}_2$  and  $\text{NiCo}_2\text{O}_4$ . However, in the transition area between each crystal particle, an amorphous phase could be observed, which is caused by the insertion of  $\text{ZrO}_2$ . Therefore, the results confirmed that  $0.5\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  has a quasi-solid solution structure. More evidence will be provided in the following section. In addition, the crystalline structures of the  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples were analyzed by powder X-ray diffraction (XRD) using  $\text{Cu K}\alpha$  radiation (Fig. 2i and j). The diffraction peaks of  $\text{NiCo}_2\text{O}_4$  correspond to the cubic phase (JCPDS No. 20-0781), and the peaks of  $\text{ZrO}_2$  correspond to the tetragonal phase (JCPDS No. 80-2155). In the XRD patterns, the typical (111), (220), (311), (222), (400), (422), (511) and (440) planes of  $\text{NiCo}_2\text{O}_4$  were observed at approximately  $18.9^\circ$ ,  $31.1^\circ$ ,  $36.7^\circ$ ,  $38.3^\circ$ ,  $44.6^\circ$ ,  $55.4^\circ$ ,  $59.1^\circ$  and  $65.0^\circ$ , respectively; the typical (110) and (112) planes of  $\text{ZrO}_2$  were observed at approximately  $29.9^\circ$  and  $50.4^\circ$ , respectively, in  $1.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$  and  $2.0\text{-ZrO}_2\text{:NiCo}_2\text{O}_4$ . The intensity of the typical  $\text{NiCo}_2\text{O}_4$  peaks, especially the peak for the (311) facet, decreased with increasing Zr content. The insertion of  $\text{ZrO}_2$  may lead to the crystal lattice of  $\text{NiCo}_2\text{O}_4$  changing. In the magnified XRD patterns in Fig. 2f, the positions of the (311) peaks slightly shifted to the left with the increase in  $\text{ZrO}_2$  content, which is similar to the change observed with Zr doping in other metal oxides [33,34], illustrating the homogeneous dispersion of Zr in the  $\text{NiCo}_2\text{O}_4$  crystal. Based on the above discussion,  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  formed a quasi-solid solution structure, even after  $\text{ZrO}_2$  crystals precipitated out of solution in the high Zr ratio samples.

To further investigate the chemical surface states of the samples, X-ray photoelectron spectroscopy (XPS) measurements were conducted. The XPS spectra of Ni 2p, Co 2p and Zr 3d are shown in Fig. S3. The binding energies of these three elements did not display obvious shifts with the changing Zr ratio. However, the intensities of the Ni and Co signals slightly decreased as the Zr ratio increased, and this decrease was partially due to the precipitated small  $\text{ZrO}_2$  particles on the surface. Additionally, the O 1s signals of the  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples were affected by the changing Zr ratio. The overlapping curves in Fig. 3a show that the O 1s signals of all  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples showed broader shoulders in the higher binding energy region, at approximately 532 eV, than the precursor, which indicates the presence of uncoordinated oxygen species. The presence of these species may be the reason for the enhanced  $\text{CH}_4$  oxidation performance after the addition of  $\text{ZrO}_2$  to  $\text{NiCo}_2\text{O}_4$ . The O 1s signals can be clearly deconvoluted into three peaks at 529.2 eV, 530.8 eV and 532.4 eV (Fig. 3b–f). The peaks at 529.2 eV and 530.8 eV can be assigned to the oxygen in the oxide lattice and oxygen vacancies, respectively [35–37]. The peak at 532.4 eV is ascribed to uncoordinated oxygen species, such as chemisorbed or dissociated oxygen or hydroxyl species, which are defect sites [38,39]. Previous research has demonstrated that surface defect sites benefit electrolyte adsorption, which can improve liquid-phase electrocatalytic reactions [17,40]. Compared to pure  $\text{NiCo}_2\text{O}_4$ , the  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples all had higher intensity O 1s XPS peaks at approximately 532.4 eV, illustrating the ability of  $\text{ZrO}_2$  to improve surface charge adsorption. The 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  sample had the largest ratio of these surface defect sites, resulting in the best  $\text{CH}_4$  electrochemical oxidation performance. Additionally, with the increase in the Zr amount, the 1.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  and 2.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples showed slight increases in the intensity of the deconvoluted O 1s XPS peaks at approximately 530.8 eV, which are related to lattice oxygen vacancies, and a decrease in the intensity of the crystal oxygen peaks at approximately 529.2 eV. These changes may indicate the  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  crystal state is affected and result in the slightly lower  $\text{CH}_4$  oxidation performance of 1.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  and 2.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ .

The working electrodes were prepared by loading the  $\text{NiCo}_2\text{O}_4$  or  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples on glassy carbon discs. The preparation details are provided in the experimental section. To investigate the electrochemical  $\text{CH}_4$  oxidation performance, a two-electrode system was employed with the working electrode as the anode, Pt foil as the cathode and a sodium carbonate solution as the electrolyte. Fig. 4a shows the linear sweep voltammetry (LSV) curves of the  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples in  $\text{CH}_4$ -saturated electrolyte. All the  $\text{ZrO}_2$  samples showed a higher current density than the pure  $\text{NiCo}_2\text{O}_4$  sample. The 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  sample showed the best performance for  $\text{CH}_4$  oxidation, not only at the onset position but also at the overall current density. In addition, the LSV curves can be divided into two steps due to the different oxidation potentials of  $\text{CH}_4$  and water. For all the  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples, the onset potential was observed at approximately 1.0 V vs. Pt, while the onset potential was approximately 1.5 V for the pure  $\text{NiCo}_2\text{O}_4$  sample. The current density gradually increased up to 2.0 V and then abruptly increased due to water oxidation. The 1.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  and 2.0- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  samples showed slightly poorer performance than 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ , which is likely due to the higher  $\text{ZrO}_2$  amount. Even though the main function of  $\text{ZrO}_2$  is to enhance the surface adsorption of carbonate ions, excess  $\text{ZrO}_2$  precipitated on the surface in the higher  $\text{ZrO}_2$  content samples and will affect charge transport during electrochemical oxidation at the  $\text{ZrO}_2$  and  $\text{NiCo}_2\text{O}_4$  interfaces, influencing the  $\text{CH}_4$  oxidation performance. The LSV curves of the 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  sample measured in Ar- and  $\text{CH}_4$ -saturated electrolytes are provided in Fig. 4b. The 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  sample showed an obviously enhanced current density in the  $\text{CH}_4$ -saturated electrolyte compared to that observed in the Ar-saturated electrolyte, demonstrating its outstanding oxidation ability for  $\text{CH}_4$  gas. Conversely, pure  $\text{NiCo}_2\text{O}_4$  did not show a better electrocatalytic ability for  $\text{CH}_4$  oxidation than water oxidation (Fig. S4), illustrating the individual

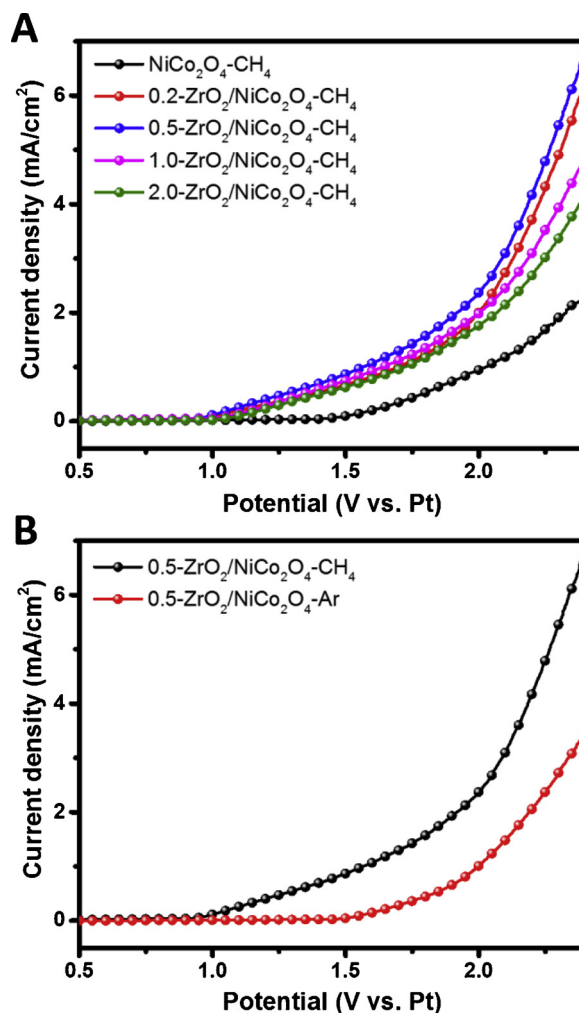


Fig. 4. (a) LSV curves of  $\text{NiCo}_2\text{O}_4$  and  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  quasi-solid-solution samples for  $\text{CH}_4$  electrochemical oxidation. (b) LSV curves of 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  for  $\text{CH}_4$  and water electrochemical oxidation.

functions of  $\text{ZrO}_2$  and  $\text{NiCo}_2\text{O}_4$  in the quasi-solid solution.  $\text{ZrO}_2$  improves carbonate ion adsorption, and  $\text{NiCo}_2\text{O}_4$  activates  $\text{CH}_4$  under a bias. In addition, when comparing the J–V (current–voltage) curves of  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  with those of conventional  $\text{ZrO}_2\text{:Co}_3\text{O}_4$  and  $\text{ZrO}_2\text{:NiO}$  samples, the superior  $\text{CH}_4$  oxidation ability of  $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  is confirmed [17].

To measure the products from  $\text{CH}_4$  oxidation, a two-electrode system was employed with catalyst-loaded carbon paper as the anode, Pt foil as the cathode and a carbonate solution as the electrolyte. The preparation and measurement details can be found in the experimental section. An electrochemical reactor under fully sealed conditions was employed, and the best catalyst (0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$ ) was selected for the experiment. A 2.0 V bias was selected as the supplementary power for the  $\text{CH}_4$  electrochemical conversion and was applied with vigorous stirring. After 5 h, 12 h and 20 h, the reaction was stopped, and the products were collected separately.  $^1\text{H}$ -NMR (proton nuclear magnetic resonance) spectra were obtained to identify the products from the 0.5- $\text{ZrO}_2\text{:NiCo}_2\text{O}_4$  catalyst after different reaction times. The  $^1\text{H}$ -NMR spectra for all reaction times are shown in Fig. 5a with the different products labelled. The  $^1\text{H}$ -NMR spectrum of the electrolyte, a sodium carbonate solution, is provided in Fig. S5 for reference. The reaction process can be analyzed over the reaction time. First, after 5 h of reacting, the main products were 1-propanol and 2-propanol with small quantities of propionic acid and acetone and negligible acetic acid [41,42]. This result was in agreement with our previous work using

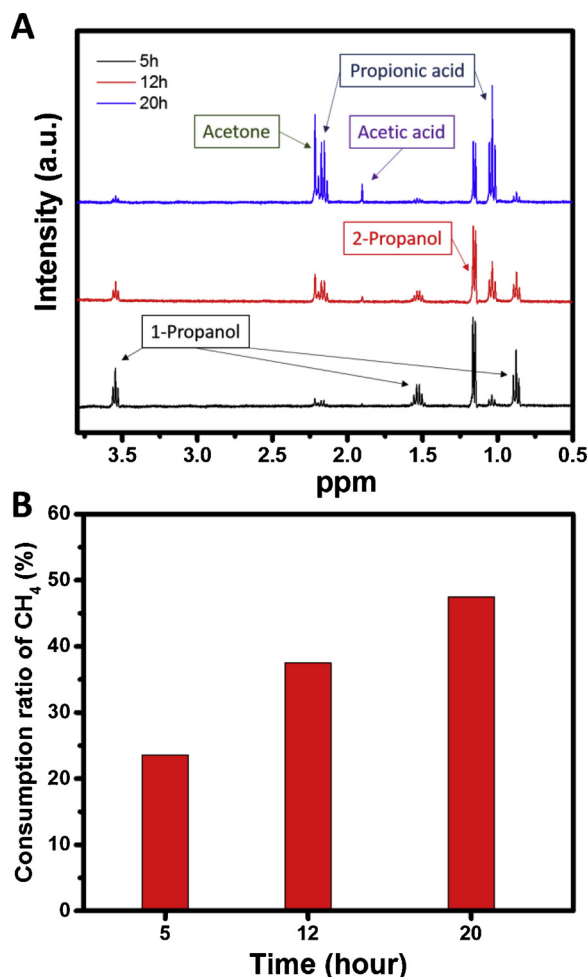


Fig. 5. (a) <sup>1</sup>H-NMR spectra of the products after 5 h, 12 h and 20 h of CH<sub>4</sub> electrochemical oxidation by 0.5-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub>. (b) The consumption ratio of CH<sub>4</sub> after 5 h, 12 h and 20 h of the electrochemical reaction.

ZrO<sub>2</sub>:Co<sub>3</sub>O<sub>4</sub> as the catalyst for CH<sub>4</sub> oxidation [17]. Then, after 12 h of reacting, the intensity of the peaks related to 1-propanol and 2-propanol decreased, and the intensity of the propionic acid and acetone peaks increased, with some acetic acid appearing at 1.9 ppm. Finally, after 20 h of reacting, the peaks related to 1-propanol and 2-propanol further weakened, and those of 1-propanol almost disappeared. The intensity of the peaks belonging to propionic acid, acetone and acetic acid greatly increased, indicating they are the terminal products of the reaction. Compared with the products observed in the <sup>1</sup>H-NMR spectra, the quantities of other by products were negligible.

To confirm the amount of CH<sub>4</sub> used in the reaction, GC (gas chromatography) was employed. The amounts of CH<sub>4</sub> consumed after reacting for 5 h, 12 h and 20 h are shown in Fig. 5b. The reference line of the CH<sub>4</sub> amount collected by GC measurements is shown in Fig. S6. After 20 h of reacting, 47.5% of the CH<sub>4</sub> gas in the sealed reactor was oxidized. In other words, the methane oxidation conversion efficiency after 20 h is 47.5%. In our previous report, acetaldehyde was the intermediate product during the CH<sub>4</sub> oxidation process [17]. However, in this process, 1-propanol and 2-propanol are the main primary products during the first 5 h of the reaction time, showing improved conversion efficiency due to the newly designed 0.5-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> catalyst. Acetic acid containing two carbon atoms was one of the terminal products after 20 h, which can be converted from acetaldehyde without further addition reactions. Moreover, the rate of propionic acid and acetone production was further increased by extending the reaction time up to 20 h, and these are the product species directly converted from 1-

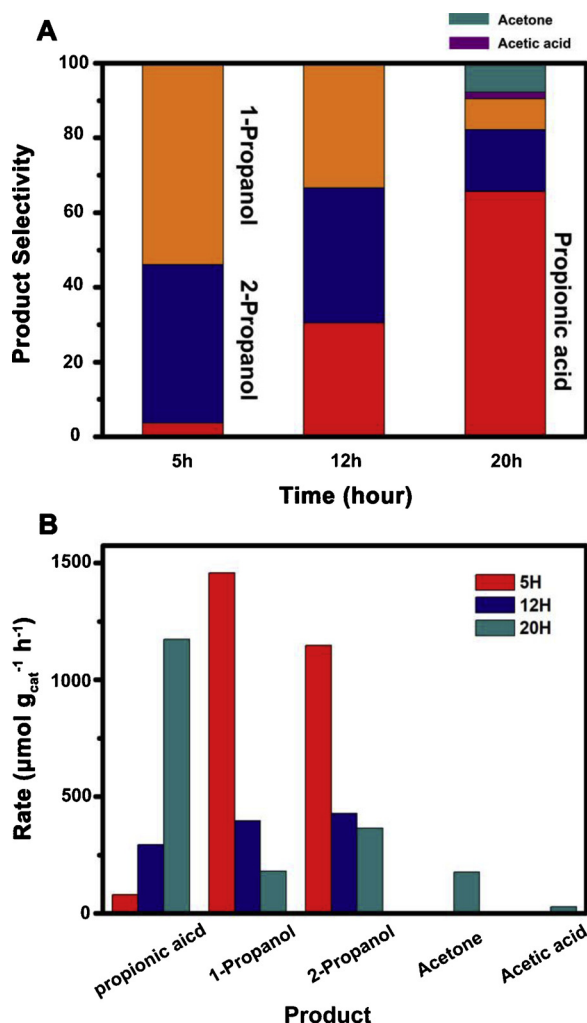


Fig. 6. (a) Product selectivity after 5 h, 12 h and 20 h of CH<sub>4</sub> electrochemical oxidation by 0.5-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub>. (b) Production rate of propionic acid, 1-propanol, 2-propanol, acetone and acetic acid after 5 h, 12 h and 20 h.

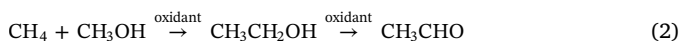
propanol and 2-propanol, respectively. 1-Propanol was almost completely consumed to form propionic acid after 20 h, which is due to the activity of 1-propanol that resulted from the radical addition process. The product selectivity with reaction time is shown in Fig. 6a, and the rate for the final main product (propionic acid) was calculated to be 1173 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> (Fig. 6b) with approximately 65% selectivity among the products, i.e., 1-propanol, 2-propanol, acetic acid, acetone and propionic acid. Reference lines were prepared from the <sup>1</sup>H-NMR spectra of standard chemicals, as shown in Fig. S7, to calculate the production rate. In order to reveal the specialty of our work, comparisons with different oxidation methods using various metal oxide catalysts has been made in terms of the product types and conversion efficiencies as shown in Table 2. In addition, products of CH<sub>4</sub> electrochemical oxidation by 0.2-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub>, 1.0-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> and 2.0-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> samples were measured as shown in Fig. S8. The production amounts by these three samples are much less than those by 0.5-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub>. But for the propionic acid, acetone and acetic acid, the production amounts were increased as a function of reaction time, illustrating that the terminal product are those three species. For the 2.0-ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> sample, very few products can be obtained even with 20 h reaction, which may due to the decreased catalytic activity caused by the excess ZrO<sub>2</sub> component.

Based on our previous report, the reaction route to produce 1-propanol and 2-propanol can be summarized as shown below [17,55,56]

**Table 2**

Comparison of methane oxidation catalysts with different oxidation methods.

No.	Method	Catalysts	Products (production rate, $\mu\text{mol/g}_{\text{cat}}/\text{h}$ )	CH <sub>4</sub> conversion (%)	Ref.
1	H <sub>2</sub> O <sub>2</sub> assisted oxidation	Fe-silicalite-1	CH <sub>3</sub> OH HCOOH CH <sub>3</sub> OOH	10.5	[43]
2	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> assisted oxidation	Fe-silicalite-1 and Cu/silicalite-1	CH <sub>3</sub> OH	10.1	
3	gaseous sulfur assisted oxidation	Au/SiO <sub>2</sub>	CH <sub>3</sub> OH	24.9	[44]
4	thermal oxidation with O <sub>2</sub>	Pd/ZrO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	16.1	[45]
5	thermal oxidation with O <sub>2</sub>	Ni/CeO <sub>2</sub>	CO	98	[46]
5	thermal oxidation with O <sub>2</sub>	Li-MgO	CO C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>6</sub>	38	[47]
6	thermal oxidation with O <sub>2</sub>	Na-W-Mn-SiO <sub>2</sub>	CO C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>6</sub>	32.7	[48]
7	CO involved oxidation	Rh-ZSM-5	CH <sub>3</sub> OH (1224) HCOOH (7753) CH <sub>3</sub> COOH (4957)	—	[49]
8	photocatalytic oxidation	Cu-0.5/PCN	CH <sub>3</sub> OH (24.5) CH <sub>3</sub> CH <sub>2</sub> OH (106)	—	[50]
9	photocatalytic oxidation	Pt/TiO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	1.1	[51]
10	photocatalytic oxidation	WO <sub>3</sub>	C <sub>2</sub> H <sub>6</sub> (2.9) CH <sub>3</sub> OH (27.1)	—	[52]
11	photocatalytic oxidation	WO <sub>3</sub> /La	C <sub>2</sub> H <sub>6</sub> (1.0) CH <sub>3</sub> OH (9.3)	—	[53]
12	photocatalytic oxidation	Zn-HPW/TiO <sub>2</sub>	CO (429)	—	[54]
13	electrochemical oxidation	ZrO <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub>	CH <sub>3</sub> CHO CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH CH <sub>3</sub> CH(OH)CH <sub>3</sub>	40	[17]
14	electrochemical oxidation	ZrO <sub>2</sub> :NiCo <sub>2</sub> O <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH (180) CH <sub>3</sub> CH(OH)CH <sub>3</sub> (363) CH <sub>3</sub> CH <sub>2</sub> COOH (1173) CH <sub>3</sub> COCH <sub>3</sub> (176) CH <sub>3</sub> COOH (27)	47.5	This work



Acetaldehyde is the first key product, which can be obtained by reacting CH<sub>4</sub>, methanol and formaldehyde via several reaction pathways. Methanol and formaldehyde are also formed from CH<sub>4</sub> oxidation. Then, 1-propanol and 2-propanol are produced through radical addition and nucleophilic addition reactions, respectively. Even with the enhanced catalyst in this work, the electrolyte with a carbonate oxidation source delivered by ZrO<sub>2</sub> was not changed. The mechanism in this work for producing 1-propanol and 2-propanol remained the same. According to the <sup>1</sup>H-NMR results, as the reaction time increased, the amounts of 1-propanol and 2-propanol both decreased due to their conversions to propionic acid and acetone. However, the rate of decrease in 1-propanol was higher than that of 2-propanol due to the higher thermodynamic stability of 2-propanol compared with that of 1-propanol. In addition, acetaldehyde, an intermediate product, is further oxidized into acetic acid after a long reaction time. The amount of acetaldehyde was insignificant because of its rapid consumption to form three-carbon-chain products. The formation mechanisms of propionic acid, acetone and acetic acid were almost the same as those for the electrochemical oxidation reactions of 1-propanol, 2-propanol and acetaldehyde, respectively. The reaction kinetics among these electrochemical oxidation reactions were different. Acetaldehyde was prior to producing propanol due to the mild oxidation conditions in our

electrochemical system. Thus, the amount of acetic acid converted from acetaldehyde was lower. Therefore, propionic acid and acetone became the main stable terminal products.

#### 4. Conclusions

We found that the ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> quasi-solid solution catalyst is an efficient electrocatalyst for CH<sub>4</sub> oxidation with a carbonate solution as the electrolyte under an ambient environment. The ZrO<sub>2</sub>:NiCo<sub>2</sub>O<sub>4</sub> quasi-solid solution anode can activate CH<sub>4</sub> molecules with the application of small biases. The high reaction rate benefited from the high electrocatalytic activity of NiCo<sub>2</sub>O<sub>4</sub>. After a long reaction time, the first intermediate, 1-propanol, was almost completely oxidized into propionic acid, and the second intermediate, 2-propanol, was converted to acetone to some extent. This new solid-solution electrocatalyst with carbonate ion adsorption and efficient CH<sub>4</sub> activation could increase the speed of the CH<sub>4</sub> to higher alcohol conversion reaction. Three-carbon-chain ketones and acids were found to be the stable and final products.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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